

UDC 666.642.1:66.046.44

REGULARITIES OF TINTING CERAMICS BASED ON LOW-MELTING CLAYS

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Translated from Steklo i Keramika, No. 8, pp. 20–21, August, 2006.

The effect of the mineral composition of low-melting red-burning clay, the gaseous medium, and the type of raw materials on the formation of light-colored (white) ceramics as a consequence of the crystallization of iron-bearing crystal phases is established.

The expanding production of decorative construction ceramics calls for the development of new technologies and mixtures which, apart from natural minerals, would contain low-cost technogenic and artificial materials.

In making ceramic facing brick, special attention is focused on developing ceramic materials of white and light colors enabling one to vary the color range by means of volume or surface tinting. White-color facing brick can be obtained from lime-rich red clay containing 12–15% (here and elsewhere weight content) carbonates or from high-grade white-burning clays. In our study we analyzed red brick clays of different mineral and chemical compositions (Table 1) to obtain light-shaded crock. These clays in addition to sand and carbonates contain 5 to 7% ferrous impurities. It is known that iron in firing can exist in two oxidation states and plays different roles in the formation of ceramic materials.

Usually 15–20% calcite in the form of chalk is added to red-burning hydromica clay to produce white-color ceramics. Decarbonization of chalk ends at temperatures above

950°C. This temperature is close to the deformation temperature of low-melting clays; therefore, the processes of decarbonizing and formation of new crystal phases are not completed, whereas hematite that has not participated in the reaction tints the ceramics. Finely dispersed calcium oxide in fired ceramics as a consequence of hydration and later carbonization may produce white tarnish on the brick surface.

Slime waste which had been generated in chemical water purification and which contained up to 95% CaCO₃ and up to 2.5% Fe₂O₃ was introduced into brick mixtures based on the considered clays. In this case the processes of sintering and crystallization occurred at lower temperatures and were more intense (Fig. 1).

The additional quantity of iron introduced via the slime, which is undesirable, was offset by more intense decarbonization of the slime and crystallization of the fired material.

It is established that decomposition of CaCO₃ in the slime starts at a temperature 70°C lower than in chalk; the process is more intense and ends at a temperature of 900–920°C. This points to the amorphous state of calcite in the slime and its enhanced reaction capacity.

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TABLE 1

Clay	Weight content, %								Mineral composition	
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O		
Vladimirovskoe, grade III (Rostov Region)	62.2	25.1	1.2	4.7	0.6	—	—	—	6.2	Kaolinite-montmorillonite
Novokubanskoe Khutorok (Krasnodar Region)	60.9	15.3	0.8	5.0	4.9	2.4	3.8	3.8	6.9	Hydromica-kaolinite with baddeleyite impurity
Gubskoe (Krasnodar Region)	54.6	14.5	0.2	7.6	2.1	6.5	3.3	1.0	10.7	Montmorillonite-hydromica
Norskoe (Yaroslavl Region)	58.0	13.5	—	7.0	8.0	4.5	3.0	3.0	7.0	The same
Taganrogskoe (Rostov Region)	6.12	11.8	1.1	7.2	5.7	2.0	2.1	0.4	8.5	"

TABLE 2

Clay	Slime content, %	Color	Compression strength, MPa	Water absorption, %	Main crystal phases
Vladimirovskoe	10	Dark pink	14.1	24.5	Mullite
	15	Pink	13.0	23.0	Okermanite
	20	Light pink	12.3	24.8	Clinopyroxene
Novokubanskoe Khutorok	10	Pink	14.5	16.6	Solid solutions of helenite
	15	Light beige	14.2	16.3	Okermanite
	20	White	14.8	18.0	Anorthite, quartz
Gubskoe	10	Light red	15.4	18.1	Bicalcium ferrite
	15	Light pink	15.0	18.7	Helenite
	20	Pink	14.2	20.0	Quartz
Norskoe	10	Dark beige	13.5	14.8	Wollastonite
	15	Beige	13.8	15.3	Solid solutions of melilite
	20	Light yellow	14.0	16.0	Quartz
Taganrogskoe	10	Pink	14.0	15.8	Quartz
	15	Light beige	14.0	16.3	Anorthite
	20	White	13.8	18.0	Wollastonite

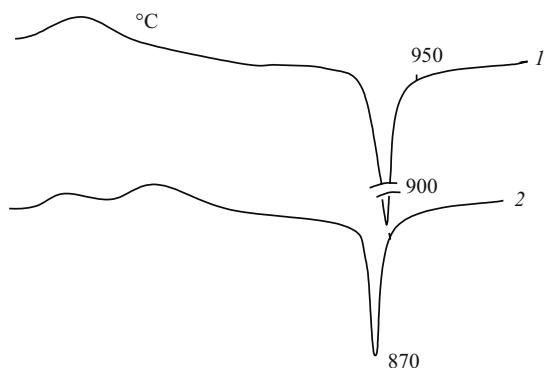


Fig. 1. Thermogram of carbonate materials: chalk (1) and high-calcium waste (2).

It is known that small quantities of active mineralizing additives in carbonate-rich ceramic mixtures influence the solid-state sintering processes. An introduction of the mineralizing NaCl additives in the form of finely dispersed common salt or LiCl (lithium-bearing chemical waste) lowers the temperature of calcite dissociation by another 60 – 70°C. At the same time, the crystallization of phases with participation of CaO and FeO perceptibly intensifies.

Mullitizing in the kaolinite-montmorillonite clay from the Vladimirovskoe deposit occurs at the firing temperature above 1050°C, and Fe³⁺ is adsorbed on the mullite crystals. The typical color of hematite in this case becomes paler. It

was not possible to achieve a white color in ceramic in this case, since mullitizing was not completed.

In an oxidizing firing atmosphere, Fe³⁺ in montmorillonite-hydromica clays does not react with other components, and the ceramics remains nonuniformly tinted.

When fired in an atmosphere with a slightly decreased oxygen content, the color of the fired material becomes lighter due to the reduction of iron to the bivalent state.

It is established that production of white and light-colored ceramics from acid montmorillonite-hydromica clays requires the crystallization of ferrous okermanite, bicalcium ferrite, wollastonite, anorthite, and mainly melilite. The process of melilite crystallization is very complicated, since the minerals of the

melilite group have enhanced tendency to the formation of solid solutions with ferrous okermanite. Therefore, in the presence of Fe²⁺ and Fe³⁺ the crystal phases have a tinting effect of a different degree. Raising the content of CaCO₃ above 20% facilitates the growth of the crystals and the formation of an excessive quantity of free CaO. The structure becomes looser and the strength decreases. The lightest-colored ceramic is obtained from mixtures with 15 – 20% CaCO₃.

The use of chlorides in mixtures intensifies the crystallization processes without decreasing the compression strength. The firing temperature of such ceramics is not higher than the clay deformation temperature and amounts to 950°C. The properties of mixtures after firing are listed in Table 2.

The decreased compression strength of the developed white (light)-colored ceramics points to the presence of free calcium oxide and high porosity. Together with undesirable carbonate salt tarnishes, this may change the exterior appearance of the brick surface, which may also be a consequence of the cement mortar diffusion in laying brick.

The optimal mixtures are those that after firing yield a white (light) colored ceramic material without a decrease in compression strength compared to ceramics obtained from pure clays.

The industrial implementation of the developed mixtures at the Novokubanskii Works of Ceramic Wall Materials has produced decorative brick that can be bulk-tinted in different colors and has also contributed to saving materials due to using waste.